

Simultaneous determination of dihydroxybenzene isomers based on thionine functionalized multiwall carbon nanotubes modified electrode

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Abstract In this article, simultaneous determination of dihydroxybenzene isomers [hydroquinone (HQ), catechol (CC), and resorcinol (RC)] was investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) at thionine functionalized multiwalled carbon nanotube (TH-MWCNTs) modified glass carbon electrode. CV and DPV results showed that the TH-MWCNTs modified electrode exhibited excellent recognition ability toward the three isomers of dihydroxybenzene. Their oxidize peak currents were linear over ranges from 9.0×10^{-7} to 3.6×10^{-4} M for HQ, from 3.3×10^{-6} to 8.1×10^{-4} M for CC and from 4.3×10^{-6} to 9.0×10^{-4} M for RC, with the detection limits of 2.7×10^{-7} , 1.0×10^{-6} , and 1.1×10^{-6} M, respectively. The proposed method would potentially be applied to multi-component analysis in environmental control and chemical industry.

Keywords Thionine · Functionalized multiwall carbon nanotubes · Dihydroxybenzene isomers · Simultaneous determination

1 Introduction

Hydroquinone (HQ), catechol (CC), and resorcinol (RC) are known as dihydroxybenzene isomers which are important environmental pollutants due to their high toxicity and low degradability in the ecological system.

Dihydroxybenzene isomers are widely used in many fields, such as cosmetics, tanning, antioxidant, dye, and photography chemicals [1]. Due to their similar structures and properties, these dihydroxybenzene isomers usually coexist and interfere with each other during their determination. Therefore, it is necessary to establish a simple, fast, and reliable analytical method for simultaneous determination of the dihydroxybenzene isomers in environmental analysis. Up to now, various determination approaches have been exploited to meet the rising demands for the determination of dihydroxybenzene isomers such as chromatography [2, 3], high-performance liquid chromatography [4], spectrophotometer [5], and capillary electrophoresis [6, 7]. However, the practical applications of these techniques are limited by relatively high cost, complicated operation, and comparatively low sensitivity. In contrast, electrochemical method is a favorable technique for simultaneous determination of them because of the advantages of facile operation, rapid response, low cost, and high sensitivity [8–12]. Nevertheless, similar chemical structures of HQ and CC lead to the adjacent potentials of redox peaks in their electrochemical signals at ordinary electrodes, so that only one or two of dihydroxybenzene isomers could be determined by electrochemical method [11, 13]. Hence, exploiting new materials to improve the sensitivity and detection limit of dihydroxybenzene isomers is still an important research topic in electrochemical analysis.

Recently, many research works have revealed that modification of electrode surface with nanomaterials is a promising avenue. Carbon nanotubes (CNTs), as one member of interesting materials of carbon family, have attracted much attention due to their unique mechanical, chemical, and electronic properties since discovered by Iijima in 1991 [14–16]. It was found that the performance of CNTs modified electrodes is superior to the performance

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of other conventional carbon electrodes in terms of electron transfer rate, reversibility, and conductivity [17–19]. Thus, CNTs have the ability to promote electron transfer reactivity when used as an electrode material in electrochemical reactions [20, 21]. However, a major limit in its application is poor dispersion of CNTs due to the large molecules with thousands of carbon atoms in an aromatic delocalized system [22–24]. More recently, this problem can be resolved by covalent and non-covalent functionalization of CNTs. These functionalized CNTs modified electrodes exhibited better water solubility and the reactivity [25–28].

Thionine (TH) is a small planar molecule with two $-NH_2$ groups symmetrically distributing on each side [29]. It was found that TH molecules had a strong interaction with CNTs, which greatly improved the water solubility of CNTs [28]. In Liu's work, TH was electropolymerized on the surface of gold nanoparticle colloidal multiwalled CNTs modified electrode (MWCNTs), which yields good performance toward the detection of adenine and guanine in DNA [30]. Shobha Jeykumari et al. prepared an enzymatic sensor based on TH covalently modified on MWCNTs to detect hydrogen peroxide [29]. Shahrokhian et al. fabricated a modified electrode based on TH-nafion supported on MWCNTs to simultaneous determination of dopamine and ascorbic acid [31]. Thus, the strategy of functionalization of CNT with TH molecules would be available for building various electrochemical sensors.

In this study, we describe a simple and highly sensitive electrochemical method for simultaneous determination of dihydroxybenzene isomers at TH functionalized multiwalled carbon nanotube (TH-MWCNTs) modified glass carbon electrode (GCE). HQ, CC, and RC exhibited three

corresponding, well-defined oxidation peaks with sufficiently differing peak potential and enhanced peak currents at the modified electrode. The proposed method would potentially be applied to multi-component analysis in environmental control and chemical industry.

2 Experimental

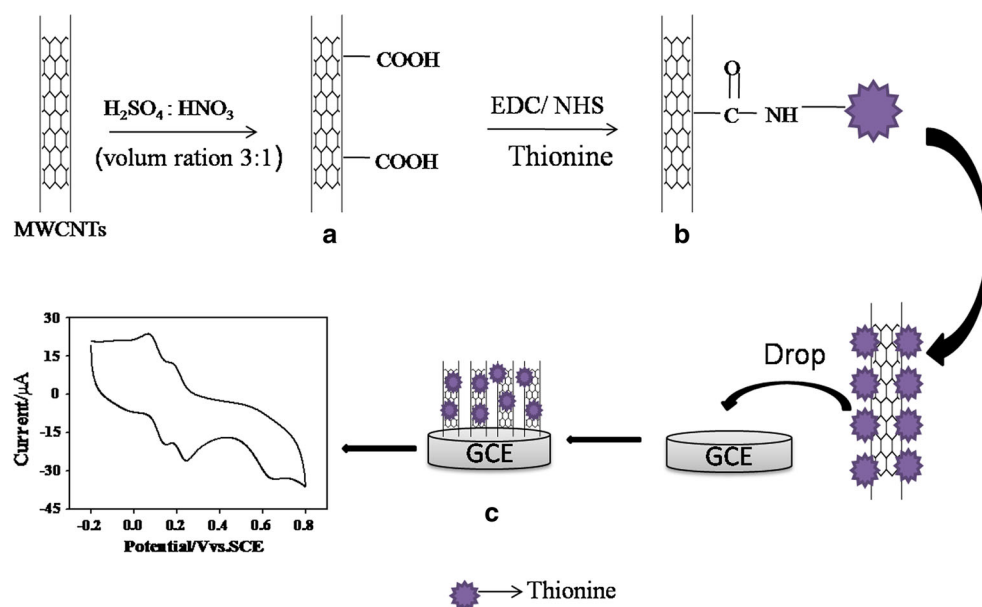
2.1 Apparatus

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed on a CHI660C electrochemical workstation (Shanghai CH Instrument, China) controlled by a microcomputer with CHI660 software. A three-electrode system was used, where a GCEs (3 mm diameter) or a modified GCE served as the working electrode, a Pt wire was used as the counter electrode and a saturated calomel electrode (SCE) served as the reference electrode. The surface morphology of TH-MWCNTs composite was characterized by scanning electron microscopy (SEM, Zeiss, Germany). The characterization of the functionalized CNTs were performed by Fourier transform infrared (FT-IR) spectrophotometer (USA). UV–vis absorption spectra were taken by absorption mode with a UV-1102 UV–vis spectrophotometer (Shanghai, China). All the measurements were carried out at room temperature (ca. 25 °C).

2.2 Reagents and solutions

The MWCNTs (diameter: 20–30 nm, length: 1–2 μm , purity: $\geq 95\%$) came from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). TH was purchased from Zhongqin

Fig. 1 Preparation of TH-MWCNTs modified GCE



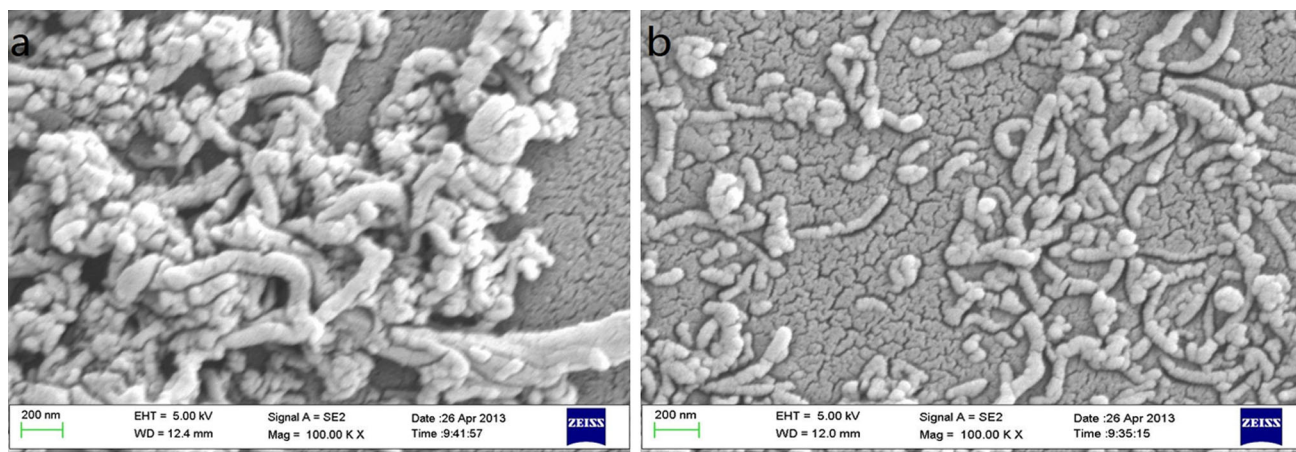


Fig. 2 SEM images of **a** carboxylic acid functionalized MWCNTs and **b** thionine functionalized MWCNTs

Chemical Reagent Co., Ltd. (Shanghai, China). 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and *N*-hydroxy sulfo succinimide (NHS) came from Shang Hai Da Rui Chemical Co., Ltd. (Shanghai, China). HQ, CC, and RC were purchased from Fuchen Chemical Reagent Factory (Tianjin, China). Potassium ferricyanide and potassium chloride (Xi'an Chemical Reagent Factory, China) were of analytical reagent grade. PBS (pH 7.0) was prepared by mixing suitable amounts of 0.1 M $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$. All the chemicals used were of analytical reagent grade, and the solutions were prepared by doubly distilled water.

2.3 Functionalization of multiwalled carbon nanotubes

2.3.1 Acid functionalized MWCNTs

The MWCNTs were purified with the following procedure: 0.2 g of the as-prepared MWCNTs sample was sonicated

in a mixture of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3:1 by volume) for a few minutes followed by refluxing under magnetic stirring at 120 °C for 4 h in oil bath, and then washed with distilled water to neutrality and dried in vacuum at 70 °C [16, 32].

2.3.2 Thionine functionalized MWCNTs

TH was attached to the broken tips of the MWCNTs using water-soluble coupling agents EDC and sulfo-NHS by forming amide linkages between the amine groups of TH and the carboxylic acid groups of the MWCNTs [29]. Briefly, 100 mg of carboxylic MWCNTs was first added into 10 mL of freshly prepared EDC solution (10 mg/mL), followed by slowly added 100 mg of sulfo-NHS and 50 mg TH with magnetic stirring. The reaction was allowed to occur at 60 °C under reflux atmosphere for 6 h with stirring. The pH of the solution was adjusted to 7 by the addition of 1 M NaOH solution. When TH were added to a

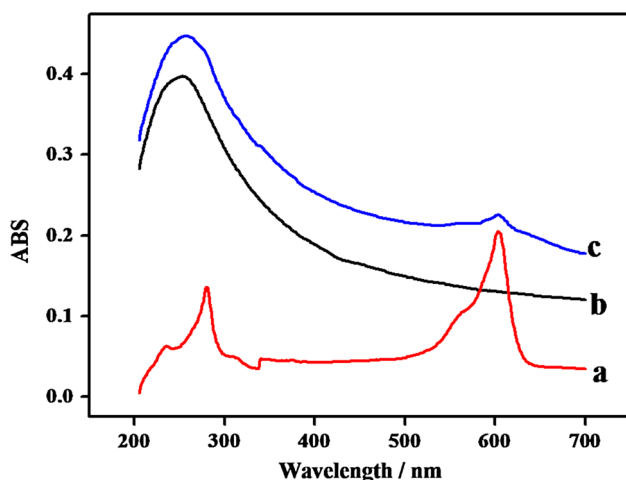


Fig. 3 UV-visible spectra of **a** thionine, **b** carboxylic acid functionalized MWCNTs, and **c** thionine functionalized MWCNTs in ethylalcohol solution

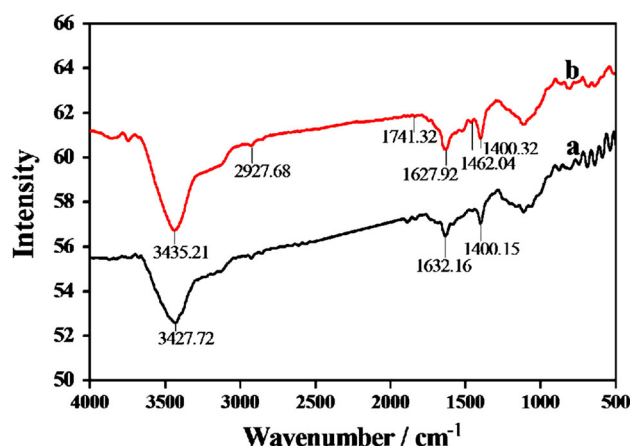


Fig. 4 FTIR spectra of **a** carboxylic acid functionalized MWCNTs and **b** thionine functionalized MWCNTs

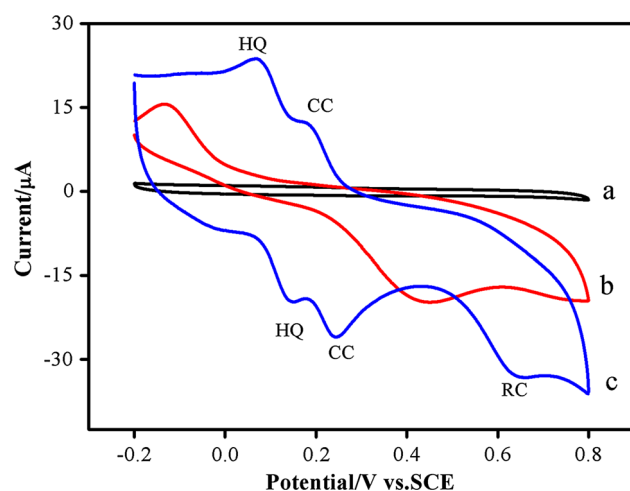
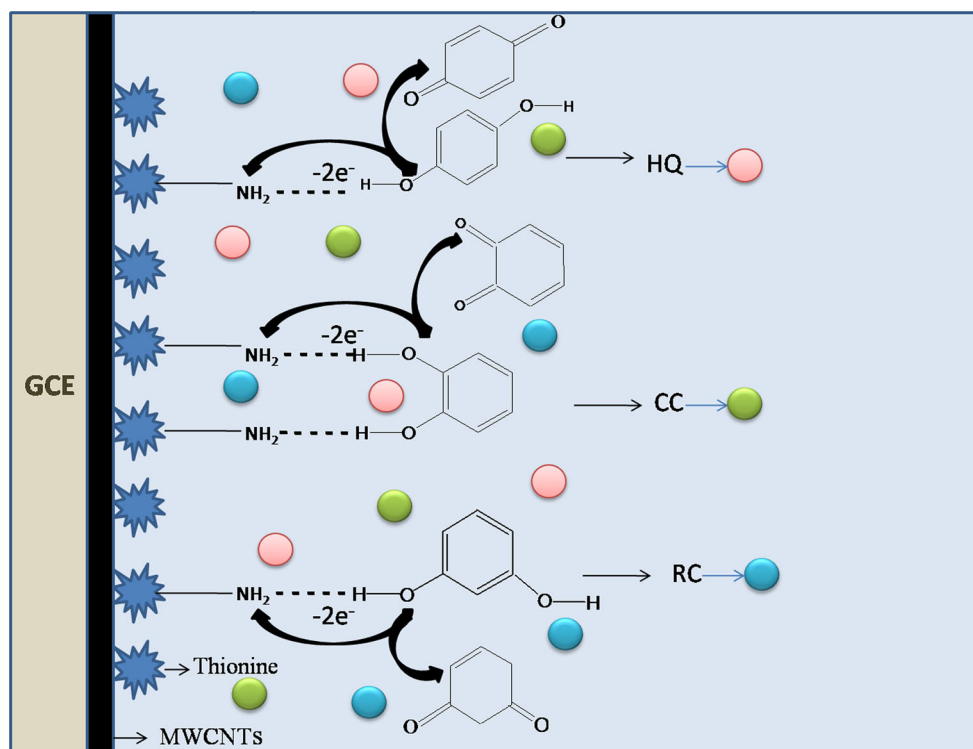


Fig. 5 Cyclic voltammograms of different electrodes: **a** bare/GCE in PBS (pH 7.0), **b** bare/GCE, and **c** TH-MWCNTs/GCE in 0.4 mM dihydroxybenzene isomers in PBS (pH 7.0), at a scan rate 0.05 V s^{-1}

MWCNTs suspension, the purple color of the solution would soon disappear in a few minutes, implying that CNTs showed a strong tendency to absorb TH molecules. Then, unreacted TH was washed thoroughly with water and ethanol. After that the products were dried in vacuum at 60°C for 12 h [28, 29].

Fig. 6 Schematic representation of the response mechanism of HQ, CC, and RC at TH-MWCNTs/GCE



2.4 Procedure

The modified electrode was prepared as reported using MWCNTs [32] or TH-MWCNTs. Before modification, GCE was polished with 0.3 and $0.05 \mu\text{m}$ alumina slurry and then cleaned ultrasonically in twice-distilled water. Soon afterward, a volume of $4 \mu\text{L}$ of 0.5 mg/mL MWCNTs or TH-MWCNTs black suspension was dropped onto cleaned GCE and allowed to dry under room temperature.

The three-electrode system was immersed in 0.1 M phosphate buffer solution (pH 7.0) containing certain amount of HQ, CC, and RC. After an accumulation on open circuit for 360 s under stirring, the voltammograms were recorded between 0.8 and -0.2 V at scan rate of 0.05 V/s . All experiments were carried out at room temperature (ca. 25°C).

3 Results and discussion

3.1 Construction of TH-MWCNTs modified GCE

Figure 1 shows the schematic illustration of the strategy used to fabricate TH functionalized CNTs modified electrode. At first, the MWCNTs were treated with $\text{H}_2\text{SO}_4/\text{HNO}_3$ to obtain carboxylic acid functionalized MWCNTs as shown in part a. Then, the carboxylic acid groups of the

MWCNTs reacted with the amine-terminated of TH by an amidation obtained TH-MWCNTs (Fig. 1b). Next, the TH-MWCNTs black suspension was dropped on the surface of polished GCE to construct the modified electrode (c), which used to detect three isomers of dihydroxybenzene.

3.2 Characterization of TH-MWCNTs/GCE

SEM was first used to characterize the morphologies of MWCNTs and TH-MWCNTs dispersed on the surface of the GCE as shown in Fig. 2. Compared with the left panel, the TH-MWCNTs are more untangled in the right panel, suggesting that the TH-MWCNTs composite has a good dispersive ability in aqueous solution and can form a well-distributed film on the surface of the electrode. Such composites are expected to be very attractive for simultaneous detection of dihydroxybenzene isomers because TH-MWCNTs can be used as an electrochemical sensing unit, yielding a high signal-to-noise ratio.

UV–visible absorption was employed to directly prove the loading of TH molecule with carboxylated MWCNTs. As shown in Fig. 3, one can see that pure TH solution has two characteristic adsorption peaks, one in visible region around 600 nm, the other located in UV region around 270 nm (curve a). The two peaks can be also observed in TH-MWCNTs solution (curve c), indicating the TH was successfully functionalized on MWCNTs. These observations are in good agreement with the earlier reports [28, 29].

FT-IR were recorded in order to identify the product of TH-MWCNTs. As shown in Fig. 4a, the appearance of peaks at 1632 cm^{-1} was attributed to the C=O , COOH stretching vibrations, indicating that C=O and COOH groups were present on the surface of the MWCNTs [29]. Curve b shows the infrared active absorption of MWCNTs functionalized with TH. The band around 1627 cm^{-1} is due to the C=O stretching vibrations of the amide I band. The peaks around $1650\text{--}1400\text{ cm}^{-1}$ for the Amide II band are assigned to the combination of N-H bending and C-N stretching vibrations formed by the covalent linkage with TH. To sum up, above results indicated that TH molecules were covalently functionalized on MWCNTs.

3.3 Electrochemical behaviors of HQ, CC, and RC

The cyclic voltammograms of a mixed solution containing HQ, CC, and RC (0.4 mM for each) at bare GCE and TH-MWCNT/GC electrode were shown in Fig. 5. At the bare GCE (curve b), there was only one broad oxidation peak at potential of 420 mV , which should be overlapped the signals of HQ, CC and RC, indicating that the three isomers of dihydroxybenzene were not simultaneously detected at bare GCE [33]. In contrast, at TH-MWCNTs/GCE (curve c),

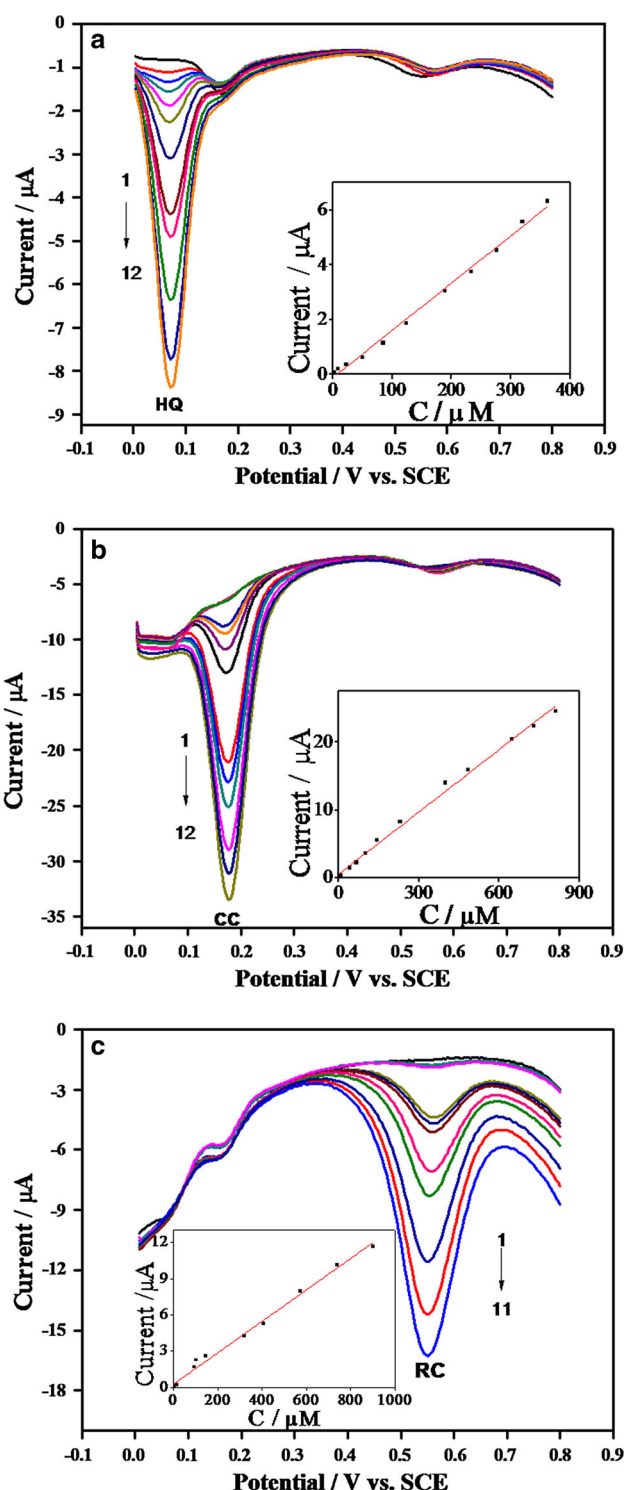


Fig. 7 DPV graphs for TH-MWCNTs/GCE in **a** different concentrations of HQ (1–12: 0.9, 3.3, 8.9, 23, 50, 85, 123, 189, 233, 276, 319, and $362\text{ }\mu\text{M}$) and containing $19\text{ }\mu\text{M}$ CC and $24\text{ }\mu\text{M}$ RC; **b** different concentrations of CC (1–12: 3.3, 8.7, 40, 67, 100, 143, 229, 399, 483, 648, 730, and $811\text{ }\mu\text{M}$) containing $33\text{ }\mu\text{M}$ HQ and $47\text{ }\mu\text{M}$ RC; **c** different concentrations of RC (1–11: 4.3, 9.7, 15, 93, 102, 145, 319, 404, 573, 739, and $902\text{ }\mu\text{M}$) containing $33\text{ }\mu\text{M}$ CC and $19\text{ }\mu\text{M}$ HQ. Insets are the calibration plots of the peak current vs. the concentration of HQ, CC, and RC, respectively, at a scan rate 0.05 V s^{-1}

Table 1 Linear ranges and detection limits of dihydroxybenzene isomers ($n = 6$)

Isomer	Linear regression equation	r	Potential (mV)	Linear range (M)	Detection limit (M)
CC	$i_p (\mu\text{A}) = 0.5738 + 0.3051c$	0.994	172	3.3×10^{-6} – 8.1×10^{-4}	1.0×10^{-6}
RC	$i_p (\mu\text{A}) = 0.2739 + 0.1298c$	0.995	560	4.3×10^{-6} – 9.0×10^{-4}	1.1×10^{-6}
HQ	$i_p (\mu\text{A}) = -0.1085 + 0.1722c$	0.992	72	9.0×10^{-7} – 3.6×10^{-4}	2.7×10^{-7}

three well-defined oxidation peaks were observed at 137, 243, and 650 mV, respectively. The oxidation peak potential difference between HQ and CC was 106 mV, CC and RC was 407 mV and it was indicated that the three isomers of dihydroxybenzene were identified completely at TH-MWCNTs/GC electrode. Moreover, in comparison with the oxidation peak currents at the bare GCE (curve a), the currents of HQ, CC, and RC (1.9×10^{-6} , 2.6×10^{-6} , and 3.3×10^{-6} A) at the TH-MWCNTs/GCE were also enhanced greatly. Thus, we could draw the conclusion that TH functionalized CNT has electrocatalytic activity for the three isomers.

The three isomers of dihydroxybenzene can be identified completely at TH-MWCNTs/GC electrode and have higher current responses. The possible reason was ascribed to the construction of the modified electrode. First, TH is a small planar molecule with two $-\text{NH}_2$ groups symmetrically distributed on each side [28]. As shown in Fig. 1b, the $-\text{COOH}$ groups of the MWCNTs reacted with the one side of amine-terminated of TH and formed amide linkages, which lead to increased the water solubility of CNTs. On the other side of TH, the $-\text{NH}_2$ groups could form hydrogen bonds with the $-\text{OH}$ groups of the dihydroxybenzenes. This essentially contributes to weaken of the hydroxyl bond energies and facilitated electron transfer through $\text{O}-\text{H}\cdots\text{N}$ as shown in Fig. 6 [34]. Second, TH-MWCNTs have plenty of edge defects to provide many favorable sites for electron transfer between the electrode and dihydroxybenzene in solution, resulting in large peak currents and low oxidation overpotentials of three isomers of dihydroxybenzene [11]. Besides, the remarkable enhancement of the peak current and the improvement of the reversibility can be attributed to the high surface area, excellent electrocatalytic activity and good conductivity of TH-MWCNTs [35]. Finally, this defects structure of the TH-MWCNTs may also have different space resistances to oxidize different isomers of dihydroxybenzenes, producing an enhanced resolution toward dihydroxybenzene isomers [11].

3.4 Determination of dihydroxybenzene isomers at TH-MWCNTs

3.4.1 Individual determination of HQ, CC, or RC in their mixtures

DPV method was used for the determination of dihydroxybenzene isomers because of its higher sensitivity and better

resolution. When the concentration of one species (HQ, CC, and RC) was changed, the others as a constant, the individual determination of the isomers in their mixtures was performed at the TH-MWCNTs/GCE first. Figure 7a was shown DPV responses of different concentrations of HQ in 0.10 M phosphate buffer solution (pH 7.0) with the constant concentrations (CC and RC) of 19 and 20 μM . The linear relationship could be established between the anodic peak current of HQ at 0.072 V and the HQ concentrations in the range from 9.0×10^{-7} to 3.6×10^{-4} M (inset of Fig. 7a). Similar behaviors were acquired for RC or CC shown in Fig. 7b and c. The regression equation, linear correlation coefficient, peak position, concentration range, and detection limit ($S/N = 3$) were summarized in Table 1. Thus, above results indicated that dihydroxybenzene isomers exhibited an excellent DPV records, proving the responses to the dihydroxybenzene isomers were relatively independent. Therefore, the proposed TH-MWCNTs modified electrode was reliable for simultaneous and quantitative determination the three isomers of dihydroxybenzene.

3.4.2 Simultaneous determination of dihydroxybenzene isomers at TH-MWCNTs/GCE

The exploit of the TH-MWCNTs/GCE for the simultaneous determination of dihydroxybenzene isomers was demonstrated

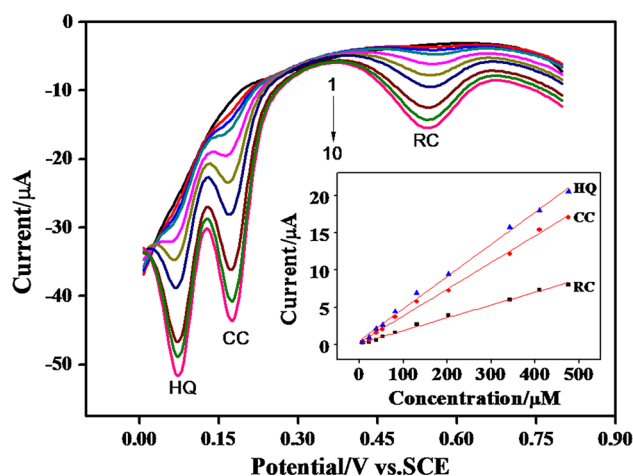


Fig. 8 DPV graphs of: 6.7, 21, 37, 52, 81, 130, 203, 342, 409, and 476 μM (from 1 to 10) of HQ, CC, and RC each. Inset linear relationship of the peak currents vs. the concentrations of HQ, CC, and RC, respectively

Table 2 Performances comparison of TH-MWCNTs/GCE with other electrodes for HQ, CC, and RC detection

Electrode	Potential (V)			Linear range (μM)			Detection limit (μM)			Reference
	HQ	CC	RC	HQ	CC	RC	HQ	CC	RC	
SWCNT/GCE	0.157	0.286	0.667	0.4–100	0.4–100	0.4–100	0.12	0.26	0.3	[1]
Nano-Au/GCE	0.212	0.312	0.711	2.5–850	1.0–650	3.0–400	0.5	0.65	0.90	[36]
AuNPs–MWCNTs/SPE	0.050	0.150	0.540	2.0–730	2.0–730	2.0–730	0.39	0.26	0.72	[37]
Nitrogen-doped CNTs/GCE	0.205	0.317	0.709	10–1,000	20–1,000	50–1,000	1.20	2.71	5.64	[15]
TH-MWCNTs/GCE	0.072	0.172	0.560	0.9–360	3.3–810	4.3–900	0.27	1.0	1.1	This work

SWCNT single wall carbon nanotubes, AuNPs Au nanoparticle, SPE screen-printed electrode

by simultaneously changing HQ, CC, and RC concentrations. As shown in Fig. 8, the peak currents of HQ, CC, and RC increased linearly with the concentrations of their own in the range from 6.7×10^{-6} to 4.76×10^{-4} M. This result proved further that the oxidation of three isomers of dihydroxybenzene occurred independently at TH-MWCNTs/GCE. The inset of illustration was calibration plots of the peak current (i) vs. concentration (c). The regression equations for HQ, CC, and RC are i_p (μA) = $0.5777 + 0.4295c$ (μM), i_p (μA) = $0.1873 + 0.1706c$ (μM), i_p (μA) = $0.3269 + 0.3564c$ (μM), with correlation coefficients of 0.995, 0.994, and 0.996, respectively. Table 2 summarized this sensor performance based on TH-MWCNTs composite and other relevant sensor materials collected from literatures. Although the linear range and limit of detection in present work are comparable to some other modified electrodes in the single dihydroxybenzene determination, we realized simultaneous determination the three isomers of dihydroxybenzene.

3.4.3 Selectivity, reproducibility, and stability of the dihydroxybenzene isomers sensor

The interferences of some common inorganic ions and organic compounds were evaluated with a mixed dihydroxybenzenes solution (HQ, CC, and RC, each 40 μM) by DPV. Measurements of the peak currents for each solution were repeated three times and average current values were obtained. The results indicated that 50-fold of Zn^{2+} , Cd^{2+} , SO_4^{2-} , Cl^- , 20-phenol, and nitrophenol had no influence on the signals of the dihydroxybenzenes isomers, with deviations below 3 %.

The reproducibility of the dihydroxybenzene sensor was carried out by six consecutive measurements at the same modified electrode. The relative standard deviations of HQ, CC, and RC were 2.06, 2.35, and 3.12 %, respectively. The stability of the modified electrode was also evaluated. It could retain 96.7 % of the original value after 40 consecutive measurements, suggesting that the modified electrode has a perfect stability and reproducibility.

4 Conclusions

In this article, the constructed TH-MWCNTs/GCE exhibited excellent recognition ability toward electrochemical oxidation of dihydroxybenzene isomers. The HQ, CC, and RC were separated entirely and three isomers can be simultaneously determined at TH-MWCNTs modified electrode. Furthermore, the modified electrode has many advantages such as high sensitivity, selectivity and stability, which may attributed to the structural and electronic properties of TH-MWCNTs. The proposed method will potentially be applied to multi-component analysis in environmental control and chemical industry.

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